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**AIR FORCE OFFICE OF SCIENTIFIC RESEARCH  
CHEMICAL AND ATMOSPHERIC SCIENCES**

**FINAL REPORT**

**F49620-01-1-0072**

**9/1/00-11/30/03**

On

Metastable Molecules in Ground and Excited States:  
Theory Development, Implementation and Applications

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## FINAL REPORT

AFOSR # F49620-01-0072

NOVEMBER, 2003

### I. OBJECTIVES

The objectives of our work for AFOSR include the following:

- Develop new theory based upon coupled-cluster theory, density functional theory, and density matrix functional theory to more accurately and easily describe the structure, spectra, and reactions of molecules.
- Implement these new methods into general -purpose computer programs, such as ACES II, to enable their routine application by non-experts to problems of their interest.
- Use these methods to provide numerical results for problems pertinent to AFOSR. These range from suggesting and exploring new rocket fuels, to plume identification and detection, to the detailed characterization of atmospheric species.

Section II highlights our recent work. The reference numbers refer to the publication list in Section III. Invited presentations at international conferences are listed in Section IV.

### II. HIGHLIGHTS OF OUR RECENT WORK FOR AFOSR

#### COUPLED-CLUSTER THEORY

Under AFOSR support we have established that coupled-cluster theory is the method of choice for most highly accurate applications of electronic structure theory for molecules. In a series of papers, 1978 (CCD), 1982 (CCSD), 1986 (CCSD[T], 1987 (CCSDT), 1992 (CCSDTQ), 1997 (CCSDTQ<sub>f</sub>), 2002 (CCSDTQP) the method has been pushed to assess its successes and limitations. Besides simply doing higher and higher categories of excitations, we also formulated and implemented the theory for the essential analytical force evaluation (1984, 1987, 1993) to permit easy determination of molecular structures, transition states, and IR and Raman spectra; excited, ionized, and electron attached states via the equation-of-motion CC methods (1984, 1992, 2001, 2003); and first and second-order properties, particularly those for NMR coupling constants (1994). In brief, we have developed the theory to the point that nearly all the properties of molecules that could be of interest are obtainable from coupled-cluster theory and the ACES II program system. The latter is widely used throughout DoD and at many universities, industrial laboratories, and super-computer centers.

- A. The current state-of-the-art in coupled-cluster theory for excited states is the EOM-CCSDT method. We first formulated and implemented it in 2001 [26]. We
- B. then generalized it to obtain ionized states [40] and then electron attached states [46]. We have illustrated these methods with application to many difficult examples. In one case, we demonstrated that the supposedly well-known vertical ionization potentials of ethylene are inconsistent because ‘vertical’  $I_p$  are not directly seen in an experiment, but are rather deduced from a high-resolution spectrum by analyzing the vibrational structure. Hence, to resolve the dilemma, we reported basis set limit EOM-CCSDT results for ethylene and define the appropriate vertical  $I_p$ ’s [48,32]. We do the same for formaldehyde and acetylene as a challenge to their experimental determination. In the near future we will take advantage of detailed theoretical spectral simulation to make our own predictions of vertical and adiabatic ionization potentials.
- C. In two efforts we considered multi-reference coupled-cluster methods that we have been developing over some years. The first addresses the current status of multi-reference CC methods compared to their much more widely applicable single reference counterparts, which have become the reference for so much of electronic structure theory[41]. The second applies nearly all the available methods we have developed, single and multi-reference, to the nearly intractable problem of  $(NO)_2$ . The problem with this system is that it is a weakly interacting, Van der Waals’ system composed of open shell fragments. This places severe demands on any method that hopes to obtain accurate values for its binding energy of  $\sim 12$  kJ/mol. However, its low-lying excited states represent some of the most difficult multi-reference ones that can be encountered. In EOM-CC all excited states derive as a response from some well-described reference states, usually the ground state. But in this case, that makes the excited state results dependent on a reasonable description of the Van der Waals’ state. As if we needed any other complication, the NO monomer has a rather large spin-orbit splitting of  $\sim 120$   $cm^{-1}$ , which considering that there are two of them, and that they are interacting, could easily account for a large portion of the 12 kJ/mol binding energy. Our study [47] applied all the MR-CC methods we have, MR-AQCC (developed by us in 1993), MR-BWCC, and double electron attached STEOM (1997), where we could describe the NO dimer from starting with two  $NO^+$  cations and adding two electrons to get to our target states. We also applied EOM-CCSDT [26]. We were able to obtain a fairly consistent treatment of the low-lying, MR excited states with the last four methods, though the more standard tools were not reliable. For the ground state itself, our best result, an extrapolated CCSD(T) value with extensive basis sets and basis set superposition corrections; was able to achieve about 7 KJ/mol of the binding energy. This system is more demanding than ozone as an essential test of any new method [47].
- D. The other primary development in CC theory is not yet published. It involves the intermediate Hamiltonian approach to multi-reference Fock Space CCSDT. We have just implemented the FS-CCSDT for the first time, but to make it useful we require the intermediate Hamiltonian to avoid problems with intruder states, which would negate FS-CCSDT’s ability to make any meaningful applications. Since the FS approach is extremely efficient for the excited states after a ground

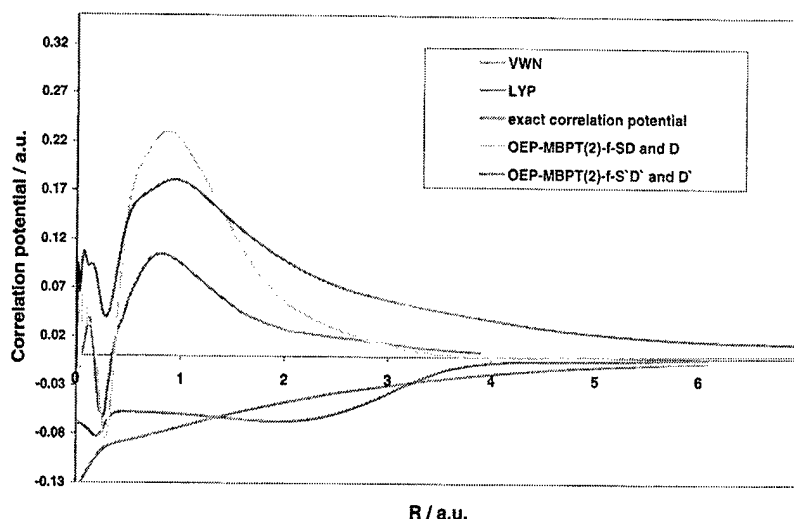
state CCSDT is performed, and since in general it offers better results than the EOM-CCSDT method; it will be a powerful approach for many excited state problems.

## AB INITIO DFT

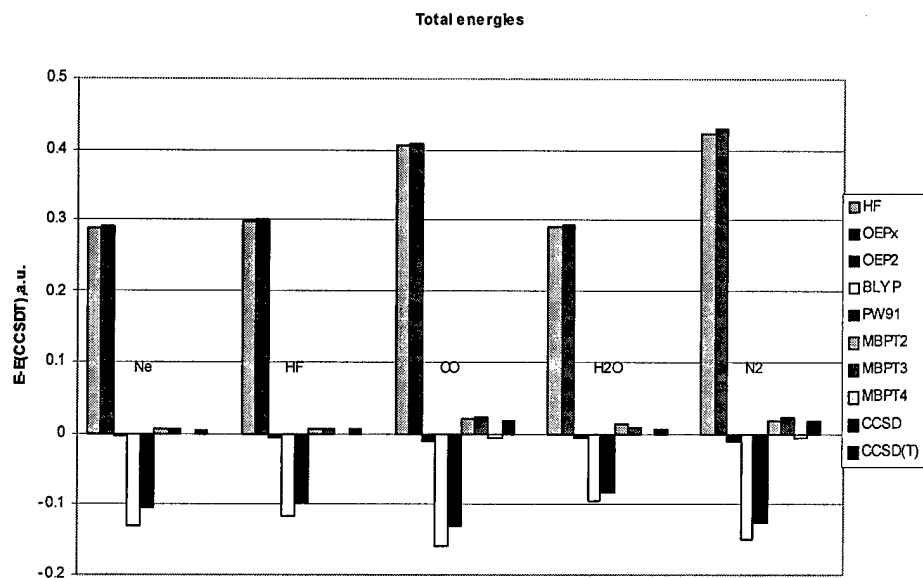
Another of our main efforts for the last grant has been our development of ab initio dft. Prior to this work, density functional theory and ab initio correlated methods as illustrated by CC theory, were considered different approaches to the same electronic structure problem. We have now changed that. It is clear from our development, which is a generalization of the so-called optimized effective potential to the correlation problem; that just like ab initio waverfunction methods, we can converge dft to the right answers. Furthermore, we have shown that by using orbital dependent expressions for the correlation energy, we can overcome the greatest weakness of ordinary dft methods is that they do not know the energy functional from which the theory starts.

- A. It is well-known that both DFT and WFT are exact, non-relativistic treatments electronic structure theory. The former has computational advantages, but suffers from not knowing the functional of the energy in terms of the density that would be necessary for an exact application. Instead, many such guesses are made giving rise to the plethora of approximations, BLYP, PW91, B3LYP, etc. Because of cancellation of errors, these actually do a decent job for molecular structure and spectra some of the time, and even local density (LDA) can often be pretty good for solids. But there is no way to know that B3LYP should be better tna LDA, etc for a given problem. This is fundamentally different from ab initio WFT methods where we know how to converge to the solution of the exact, non-relativistic Schrodinger equation. In ab initio dft we instead use orbital dependent functionals that are known to be right to some order of perturbation theory, or even at the non-perturbative, CC limit. In the figure we show how good the potentials we generate from ab initio dft are compared to reference results from quantum Monte Carlo for the Ne atom[49]. Note how bad the other correlation potentials are for the standard DFT approximations, which even have the wrong sign. It is not surprising that such poor representations of the potential cause poor numerical results.

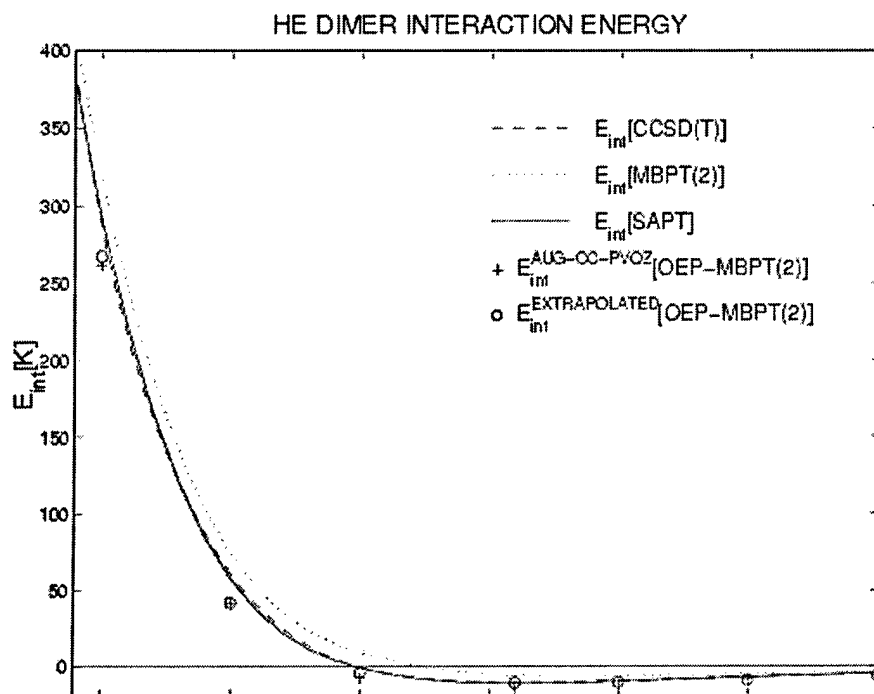
Correlation potential of neon (Roos-ATZPU basis set) (2)

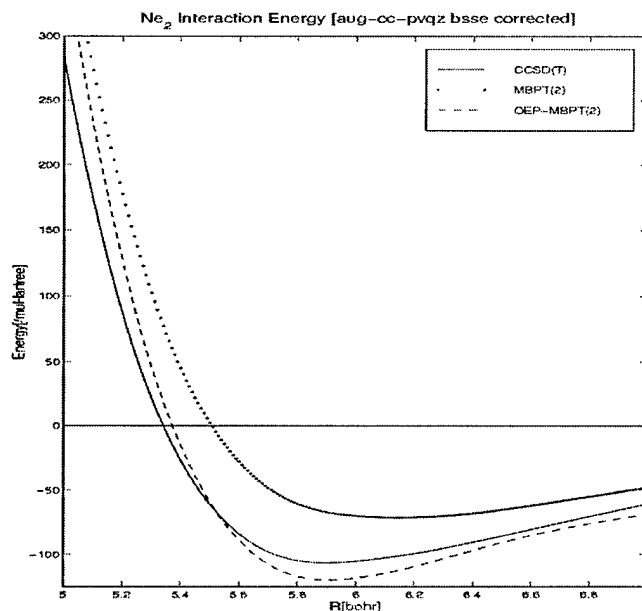


- B. The fusion of DFT and WFT in ab initio dft gives rise to a whole series of approximations that *converge to the right answer* unlike other DFT methods. The first of these approximations is what we obtain from second order perturbation theory, OEP-MBPT(2)[31, 49]. As shown in the following figure (the third result from the left, where zero means no error), the accuracy of the method is almost that of CCSD(T), the most accurate, widely applicable theory at our disposal today. Whereas the latter is an  $\sim n^7$  method, OEP-MBPT(2) is an iterative,  $\sim n^5$  computation, making it possible to potentially achieve CC accuracy in a more attractive computational procedure. That, plus putting DFT onto a equal footing with ab initio WFT, is what makes this approach so exciting.



- C. Finally, the bane of all DFT methods is their inability to describe weak interactions. The following figure shows how well we do for  $\text{He}_2$  and  $\text{Ne}_2$  with OEP-MBPT(2). Note the virtual agreement of OEP-MBPT(2) with CCSD(T). This is unprecedented in DFT circles.





## NMR COUPLING CONSTANTS

With the emphasis of the HEDM program on the various kinds of spectra for molecules, including those in the condensed phase; such as atom embedded into cryogenic hydrogen, etc; we first addressed NMR coupling constants a few years ago, when it became clear that there was an unsolved problem in theory's ability to provide reliable results. We traced the problem to (1) the frequent exclusion of some of the four terms involved in the coupling constant, demonstrating that the Fermi contact, paramagnetic spin-orbit, spin-dipole, and diamagnetic spin orbit terms were all important for some cases. In particular, it is virtually meaningless to attempt to obtain correct coupling constant involving fluorine unless all are included. Next, (2) we showed that only with a high level of correlated theory, namely EOM-CCSD, could we adequately describe the essential effects of electron correlation. Finally, (3) we did sufficient basis set tests to deduce that EOM-CCSD with a proper basis provided a predictive method for NMR coupling constants with a mean error of about 3 Hz. Armed with that tool we resolved long term discrepancies in the literature for non-classical carbocations like the ethylcarbonium ion (1995) and the norbornyl cation (1996).

The next major development was the recognition from experimentalists that the two-bond coupling between heavy atoms bound by a hydrogen bond could be observed[2], with all its ramifications for biological structure determination. With our predictive tool, we could address problems like how the coupling constants depended upon distance and determine a 'universal' curve for all N-H-N couplings, eg [12,28]. This was further generalized to apply to C-H-N constants where we also considered the hybridization at the C atom [44] and other constants. This provides a tool to compliment X-ray structure determination, eg.

- A. In the past year we have focused on generalizations of two-bond coupling for H-bonds, such as those between F-H-N[42, 43]. As in all systems containing F, it is



impossible to expect to accurately describe these constants without the full set of terms contributing to coupling constants. Otherwise, several dramatic examples of misleading results occur. In these two papers we explore both the neutral and the cation complexes. As we found for N-H-N, both can be fit to the same curves, though not as easily as in the N-H-N case.

- B. For C-H-N constants, the hybridization on the C atom is essential to obtain the kind of predictive results of coupling constants with distance that we observed with N-H-N. This, however, provides us with another tool of great use to experimental understanding, since our results will distinguish which hybridization form C is in. This offers a new way to assess whether the C atom in question is single, double, or triple bonded.
- C. We also addressed the long-term supposition that the magnitude of the coupling constant was related to the co-valency of its bond. By controlling the dipole moment of prototype covalent and ionic systems to offer a measure of the covalent bonding, we then determined the coupling constants and demonstrated conclusively that there was no relationship between the two[Book Chapter, 2].

We, of course, did many other things during this reporting period. Many of these dealt with our joint DARPA-AFOSR study of poly-nitrogens as potential HEDM fuels. These will be the subject of our other annual report for AFOSR, so will not be discussed here. Other work is apparent from a perusal of the attached publication list. Furthermore, we also presented many invited presentations at international meetings. See attached list. Our many invitations to speak at meetings throughout the world is another testament to our role in the field and the interest in our new research results. Finally, the Science Foundation of Ireland awarded RJB an E. T. S. Walton Fellowship, which enabled him to spend four months in Ireland developing new research interests and collaborations that will benefit our AFOSR work in the future.

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48. M. Musial, R.J. Bartlett, "EOM-CCSDT study of the low-lying ionization potentials of ethylene, acetylene and formaldehyde." Chem. Phys. Letters, in press.

#### PUBLICATIONS PENDING

49. R. J. Bartlett, I. Grabowski, S. Hirata, and S. Ivanov, THE EXCHANGE-CORRELATION POTENTIAL IN AB INITIO DENSITY FUNCTIONAL THEORY, submitted, Phys. Rev.
50. T. Henderson, R. J. Bartlett, "Short-range Corrections to the Correlation Hole" Phys. Rev. A, submitted, Phys. Rev.

#### INVITED LECTURES AT PROFESSIONAL CONFERENCES (LAST 3 YEARS)

- September 2003 – "Metastable Molecules in Ground and Excited States," 2<sup>nd</sup> Advanced Energetics Technical Exchange, Aberdeen, MD
- September 2003 – "Coupled-cluster Methods and Their Applications to Energetic Molecules," 226<sup>th</sup> ACS National Meeting, New York, NY
- August 2003 – "High level Couple Cluster Theory: What Did We Learn?" 8<sup>th</sup> European Conference on Quantum Systems in Chemistry and Physics, Spetes, Greece
- July 2003 – "Ab Initio Density Functional Theory," Electron Correlation: Ab initio Methods and Density Functional Theory, Satellite Meeting of the XIth International Congress of Quantum Chemistry, Bad Herrenalb, Germany
- April 2003 – "Frontiers in Theoretical Chemistry," a Symposium in Honor of Prof. Rudolph A. Marcus, Los Angeles, CA

March 2003 – “From Wave Function Theory to Density-Functional Theory and Back,”  
225<sup>th</sup> ACS National Meeting, New Orleans, LA

October 2002 – “Scalable Software for Computational Chemistry,” University of  
Kentucky, Lexington, KY

September 2002 – “Predictive Theory from Molecules to Materials,” Science at the Edge,  
Michigan State University

July 2002 – “Advances in Electronic Structure Theory: Current Trends and Future  
Prospects,” ICTCP-IV, Marly-le-Roi, France

June 2002 – “Predictive Theory from Molecules to Materials,” Symposium to Initiate  
Joint Ph.D. Program between France and the United States, Strasbourg, France

June 2002 – “The Exchange Correlation Potential in *ab initio* DFT: What Does the  
‘Right’ Exchange Correlation Allow Us to Do?” CECAM Workshop, Lyon, France

April 2002 – “Speculation on High Nitrogen Molecules,” BMAED Committee on  
Advanced Energetic Materials and Manufacturing Technologies, Washington, DC

April 2002 – “Advances in the Treatment of Electron Correlation in Molecules: Coupled-  
Cluster Theory and *ab initio* DFT,” 223<sup>rd</sup> ACS National Meeting, Orlando, FL

January 2002 – “Predictive Theory from Molecules to Materials,” University of  
Tennessee Chemicals Physics Workshop, Knoxville, TN

October 2001 – “Modern Aspects of Many-Electron-Theory,” WE-Heraeus-Seminar, Bad  
Honnef, Germany.

September 2001 – “Ab Initio DFT,” WOG – Density Functional Theory, Brussels,  
Belgium.

September 2001 – “Ab Initio DFT,” 9<sup>th</sup> International Conference on the Applications of  
the Density Functional Theory in Chemistry and Physics, San Lorenzo de El Escorial,  
Madrid, Spain.

September 2001 – “Ab Initio DFT,” Austrian – Czech – Polish – Slovak Symposium on  
Quantum Chemistry, Ustron-Jaszowiec, Poland.

August 2001 – “Polynitrogen molecules that don’t exist that should,” DARPA  
HEDM/NANO Workshop, Rosslyn, VA.

July 2001 - “Ab Initio Density Functional Theory,” Molecular Quantum Mechanics: The  
Right Answer for the Right Reason, An International Conference in Honor of  
Professor Ernest R. Davidson, Seattle, WA.

June 2001 - “Electron correlation in Molecules and Polymers: From Coupled-Cluster  
theory to Ab Initio DFT,” The 2<sup>nd</sup> International Workshop on Electron Correlations  
and Materials Properties, Rhodes, Greece.

May 2001 - “Ab Initio DFT,” AFOSR Molecular Dynamics/Theoretical Chemistry  
(MD/TC) Contractor's Meeting, Irvine, CA.

- December 2000 - "Ab Initio Density Functional Theory," PACIFICHEM (2000 International Chemical Congress of Pacific Basin Societies), Honolulu, Hawaii, December 14-19, 2000.
- October 2000 - "Prospects for Polynitrogen HEDMS," DARPA Polynitrogen HEDM Program, Salt Lake City, UT, October 27, 2000.
- October 2000 - "New Developments in Theory and their Applications to HEDM's," 2000 Air Force High Energy Density Matter (HEDM) Contractors Conference, Salt Lake City, UT, October 24-26, 2000.
- July 2000 – "Ab Initio Density Functional Theory," 4<sup>th</sup> Canadian Computational Chemistry Conference, Bishop's University, Lennoxville, Québec, Canada
- May 2000 – "Predicted NMR Coupling Constants Across Hydrogen-Bonds: A Fingerprint for Specifying Hydrogen Bond Type?," SETCA 2000, University of Georgia, Athens, GA.
- May 2000 – "Ab Initio Density Functional Theory," Twelfth Annual Workshop on Recent Developments in Electronic Structure Methods," Georgia Institute of Technology, Atlanta, GA.
- May 2000 - "Predicted NMR Coupling Constants Across Hydrogen-Bonds: A Fingerprint for Specifying Hydrogen Bond Type,?" Morley Award Symposium for Isaiah Shavitt, Cleveland, OH.